Title of the Synopsis :

Analytical Studies on Some Domiciliary Lethal Pesticides in Various Agricultural, Biological and Environmental Samples.

Introduction :

The term pesticide covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, plant growth regulators and others (1). Domiciliary means household usable. Domiciliary lethal pesticides are chemicals used for preventing ,destroying or controlling the pest , parasites, vectors of human or animal and plants diseases .Epidemiological studies indicates that, despite premarket testing, current exposures of pesticides are associated with risks to human health has been increasing because of there inherent toxicity and wide spread use, the domiciliary to public health, particularly lethal pesticides possess a serious threat to public health, specially to infants and children(2).These are generally used either as sprays, liquids, sticks, powder, crystals, balls, coils and folques etc. Since then there have been hundreds of scientific studies done on all continents to determine if there is a relationship between pesticide use and human health problems. Various studies shows that the year wish consumption of domiciliary lethal pesticides, including all type of pesticides is increasing rapidly and also resulting many hazardous diseases too.

It has been estimated that around one-third of the crop production would be lost if chemical substances were not applied against pests (3). Pesticides have also been used in non-agricultural sectors such as wood preservation, disinfection or household uses. Inspite of the several advantages, some pesticides can be toxic to humans and animals and their continuous application is causing serious problems of environmental and food contamination. Every legislation in this area covers not only the conditions concerning the placing of pesticides on the market but also the levels of pesticide residues allowed in waters and food as well as the actions needed to promote sustainable use of pesticides. Many new and some old modified chemicals are introduced in the market in order to kill mosquito, flies, rodents, insects, at homes and Indoor working environment i.e for domiciliary purposes. These chemicals are generally used as domiciliary lethal pesticides (table-I)(4).All these types of domiciliary lethal pesticides are very toxic and cause oncogenic and carcinogenic diseases in human body (5)

There are many sources of exposure to pesticides. Various routes of exposure for pesticides are oral ingestion, dermal absorption, and inhalation. Lawn and garden pesticides are used in homes and gardens, on golf courses, along highways and hydro rights of way, and in public parks, exposing people by all routes. Pesticides can be tracked into homes, or brought home from work on clothing and in vehicles, exposing family members as well. Pesticides are used in pet, in treatments for scabies and lice, and for home infestations of wasps, cockroaches, and ants. Agricultural pesticides are used on farms, greenhouses, and orchards, and consumers eating produce and other food products ingest them. Pesticides used domestically or in agriculture run off into ground and surface water, exposing entire populations. Parents track pesticides indoors on their shoes,

inadvertently exposing their children . Some pesticides that degrade outdoors in sunlight are more persistent once they are present indoors. (6)

There are numerous health effects on human due to domiciliary lethal pesticides. The most frequent reported health outcomes were neurological symptoms (40%), including headache and dizziness, respiratory symptoms (40%), including upper respiratory track pain and irritation and gastrointestinal symptoms (35%), and including nausea and vomiting. One of five likely suspects explaining why farmers had elevated risks of several forms of cancer including Hodgkin's disease, multiple myeloma, leukemia ,melanoma and cancer of the lips(7).

Various epidemiological studies indicate that, despite premarket testing current exposures are associated with risk to human health. Better understanding of the patterns of exposure, the underlying variability within the human population, and the links between the animal toxicology data and human health effects will improve the evaluation of the risks to human health posed by pesticides (8). These pesticides study indicated a child's risk of developing non-Hodgkin lymphoma was similar for both maternal exposure to pesticides during pregnancy and direct exposure to domiciliary lethal pesticides. The use of domiciliary lethal pesticides increased the risk of lymphoblastic lymphoma also (9)

Many researches have found that people with high level of pesticides and chemicals in their blood streams are far more likely to develop genetic mutations linked with cancer of the pancrease .One of the latest epidemiological studies performed in Spain between 1999 to 2009 shows that among a total of 2,661 cases of breast cancer reported in female population 2,173 (81%) were observed in areas of high pesticides contamination (10).

CONSUMPTION OF PESTICIDE IN INDIA

The major part of the Indian economy do consist of agriculture, also considered as the backbone for it. As about 65% of the population depend on agriculture for their livelihood and thus exposed to chemical pesticides. India is the fourth largest pesticide producer in the world after the U.S., Japan and China. Domestic consumption is found to 39 thousand metric tones (TMT). The production of Indian pesticide industry has almost remained stable at 82000-85000 MT during financial year 2010.(11)

CONSUMPTION OF PESTICIDE IN CHHATTISGARH

The annual consumption of indigenously produced pesticides in Chhattisgarh state for year 2003-04 , year 2004-05, year 2005-06, year 2006-07, year 2008-09, year 2009-10, year 2010-11 are 377.36 M.T. , 415.88M.T,449.30M.T. , 487.05M.T, 400.00M.T, 410.00M.T and 570.00M.T and 2011-12 is 600.00M.T. respectively and demand 2012-13 is 800 M.T. (12).

A Brief Review Of The Work Already Done In The Field :

Many analytical methods are available for the determination of domiciliary lethal pesticides include Gas Chromatography /Mass Spectroscopy (10-12) ,Sorption and Desorption(13), Quantum Dot Film Biosensor (QDFB) (14), Electrospray ionization integrated in Liquid Chromatography tendam Mass Spectroscopy (ESI-LC)(15),Thermal Desorption based ambient Mass Spectroscopy (TDAMS)(16),Liquid Chromatography Mass Spectroscopy (LC-MS)(17),Atmospheric Pressure Chemical Ionization (APCI)(18),Time of Flight Mass Spectroscopy (TOF-MS)(19), Fluorescence Polarization immune assays (FPIA)(20), Liquid phase micro extraction(2010) etc. Most of the currently employed instrumental methods are most expensive, quite elaborate, require expensive instruments, maintenance needed, too sophisticated for field measurement and are difficult to be used in the routine analysis of different matrices**.**

Objectives :

- Development of new sensitive, selective, cheaper and refine spectrophotometric method for the detection and determination of various domiciliary pesticides in various agricultural, biological and environmental samples.
- Sample is to be prepared by extraction of pesticide using an efficient and selective solvent followed by clean-up procedures to remove interfering species.
- Determination of the level of pesticide residue qualitatively and quantitatively with their breakdown products in the cleanup extracts using simple sensitive and selective spectrophotometric method will be done as an alternative of costly sophisticated instrumental techniques.

Noteworthy Contribution In The Field Of Proposed Work :

Earlier some work has been already done at School of Studies in Chemistry Pt. Ravishankar Shukla University, Raipur, Chhattishgarh. Simple and sensitive spectrophotometric methods , Thin layer chromatography, Solid Sorbent System and Low cost monitoring methods has been developed for the detection/determination of some toxic pesticides in various agricultural, biological and environmental samples.

A new spectrophotometric determination of methyl parathion using guaiacol as a new coupling reagent is described. The method is based on the reduction of nitro group present in methyl parathion with zinc/ HCl to form amino methyl parathion. The dye shows an absorbance maxima at 470nm and obeys Beer's law in the range of 18 - 200µg methyl parathion in 25ml final solution (0.6 - 8ppm). The important analytical parameters and optimum reaction conditions have been evaluated. The method has been successfully applied to the determination of Methyl parathion in soil and various vegetable (21).

A new and sensitive method for the determination of widely used acaricide kelthane or dicofol is described. The method is based on the modification of fujiwara reaction reported for the determination of polyhalogenated hydrocarbons kelthane on alkaline hydrolysis give chloroform which can be determined by fujiwara reaction. In the present method the pink colour obtained in the above reaction is discharged with a few drops of glacial acetic acid followed by the addition of sulfanilic – formic acid, reagent which gives an orange coloured polymethine dye. The modification increase the sensitivity five fold than other earlier reported fujiwara reactions. Beer's law is obeyed in the range of 1.48 – 11.8 ppm of kelthane. The method is free from the interference of other organochlorine pesticides and can be successfully applied for the determination of kelthane in water, milk and vegetable (22)

A sensitive spectrophotometer method for the determination of a widely used herbicide, paraquat has been developed. Paraquat is reduced with glucose in an alkaline medium and the blue coloured ions obtained has been measured at 600 nm. Beer's law is obeyed in the range of 0.1 – 1.2 ppm of paraquat . The molar absorptivity is found to be 1.26×10^5 l mol^{-1} cm^{-1}. The standard deviation and relative standard deviation are found to be $\pm$ 0.007 and 2.0% respectively for 5 µg per 10 ml of paraquat analysed over a period of 7 days. The method is free from the interference of other commonly used pesticides and metal ions. The application of the method, for the analysis of paraquat in plants, fruits, grains, water, blood and urine has been reported (23).

A new sensitivity spectrophotometric method is developed for the determination of carbofuran, a widely used carbamate pesticide, at sub ppm level. The method is based on the hydrolysis of carbofuran under alkaline condition to carbofuran phenol (2,3-dihydro-7 hydroxy-,2-dimethyl benzofuran) and then the subsequent coupling of the phenol with p-anisidine and N- chlorosuccinimide in the presence of a catalyst (ie. A mixture of sodium nitropruside and manganese dioxide).The greenish-blue dye formed obeyed Beer's law in the range of 0.1 to 1.2ppm of carbofuran. It has molar absorptivity 1.9×10^5 ($\pm$100) l mol^{-1} cm^{-1} and has the maximum absorbance at 660nm.The method is simple, sensitive and free form the interference of other common pesticides and ions. The method has been successfully applied to the determination of carbofuran in polluted water, soil, foliages and biological samples .It is also compared with other recently reported spectrophotometric methods(24).

A new spectrophotometric determination of parathion using 1-napthol as a new coupling reagent to form an azo dye is described .The method is based on the reduction of nitro group present in parathion with Zinc/HCl to form an amino derivative . The amino parathion thus formed is diazotized and subsequently coupled with 1-napthol to form an orange coloured azo dye in alkaline medium .The dye shows an absorbance maxima at 500nm and obeys Beer's law in the range of 0.4-3.3ppm of parathion .The

important analytical parameters and optimum reaction conditions have been evaluated .Methyl parathion, an analogue of parathion, can so be determined by this method .The method has been applied for the determination of parathion in soil and various vegetables(25).

The proposed method for the determination of Y- BHC (lindane) is based on the extraction of Y- BHC from water by means of activated charcoal followed by the dechlorination Y- BHC to Benzene by zinc and acetic acid in a new simple apparatus. The Benzene thus formed is drawn into nitrating mixture to form m-dinitro benzene, which is reduced to m-phenylene–diamine , diazotized and subsequently coupled with N(1-naphthyl) ethylene diamine dihydro chloride to form a purple coloured dye having maximum absorbance at 540 nm. The Beer's law is obeyed in the range of 0.3 to 2.4 ppm of Y- BHC. The optimum reaction condition and other analytical parameters have been evaluated and successfully applied for the determination of Y- BHC in river water, stream water, soil and various cereals (26).

A new and highly sensitive spectrophotometric method was developed for the determination of widely used organophosphorous insecticide chlorpyrifos. The method is basedon alkaline hydrolysis of chlorpyrifos to 1,2,4-trichlropyridine, followed by coupling with diazotized p-aminobenzoic acid in alkaline medium. The absorption maxima of the wine red dye compound formed ws measured at 520nm. Beer's law was obeyed over the concentration range of 1.2 to 18µg in final solution volume of 25ml (0.048- 0.72ppm). The molar absorptivity, Sandell's sensitivity and correlation coefficient were found to be 1.8 x 104 (+100) mole-1 cm-1, 0.011µg cm-2 and 0.9989, respectively. The standard deviation and relative standarddeviation were found to be ±0.005 and 2.02% respectively. The method was simple sensitive and free from interferences of other pesticides and diverse ions. Other organophosphorous pesticides did not interfere with the proposed method. The method was satisfactorily applied to the determination of chlorpyrifos in environmental and biological samples.(27)

Proposed Methodology :

1. Detail survey of extensively used domiciliary lethal pesticide in selected agricultural, biological and Environmental samples.
2. Literature survey will be performed to obtain the analytical method developed, identifying the demerits existing in the reported experiments.
3. Sampling of various toxic pesticides from different selected areas will be done.
4. Collected samples will be then treated in laboratory as required.
5. Analysis of various sample and to identify different insects killer used in various areas, to identify and determine the level of domiciliary lethal pesticides used .Also attempts will be made to measure the relative exposure of humans to domiciliary lethal pesticides.

6. The study will be conducted to identify the inert ingredients present in domiciliary lethal pesticides responsible for causing toxicity.
7. Simple Spectrophotometric analytical method will be developed to find out the pesticide concentration level in various agricultural, biological and environmental samples.
8. Development of new simple and sensitive spectrophotometric method using , indicator tube ,test paper ,solid sorbent system , thermo gravimetric thin layer chromatography system for the detection and determination of various classes of domiciliary lethal pesticides such as : Organophosphate , Organochlorine ,Carbamate , pyrethroids and Rodenticide etc will be done.
9. Optimization of analytical parameters like pH, reagent concentration, temperature and diverse ion effects etc.
10. Study of statistical parameters *viz*. standard deviation, relative standard deviation, correlation coefficient, molar absorptivity, sandell's sensitivity etc.

Expected Outcome of the Proposed Work :

- The expected method is simple and more sensitive than other spectrophotometric method reported for the determination of domiciliary lethal pesticides.
- The expected method will be successfully applied for the determination of domiciliary lethal pesticides in water, soil, food and biological sample.
- The practical scientific advantage of the proposed research work is to introduce awareness to the common people as well as other agencies to understand the health effect to the contamination of toxic pesticide in water, soil, and biological system.
- The expected method will be compared with other spectrophotometric method which will be rapid cheaper and good alternative of other costly and mostly sophisticated instrumental methods and low cost might be preferred in small laboratory.

Table-1 : The Chemicals are generally used as Domiciliary Lethal Pesticides.

S.No	Chemical Name	Classification	LD_{50} value mg/kg(rat) oral/dermal	Toxic Effects
1.	Chlorpyrifos	Organophosphate	95 to 270	Nausea, Endocrine disrupter, affect the central nervous system, the cardiovascular system, and the respiratory system
2.	Alpha cypermethrin	Pyrethriods	187 to 326	Affects the central nervous system (brain and spinal cord) causing writhing, salivation and clonic convulsions .
3.	Premethrin	Pyrethriods	50/250	Nausea, Headache, Muscle weakness, Block calcium magnesium ATPase
4.	Buprofezin	Thiodiazin	2198	Carcinogenic, skin and eye irritation ,allergic.
5.	Borax	Carbonate	869-1271	Respiratory and skin irritation, Diarrhea,Kidney failure.
6.	Propargite	Unclassified	2639	carcinogenicity, reproductive and developmental toxicity, neurotoxicity, and acute toxicity.
7.	Aldrin	Organochlorine	39-64	Produce tremors, hyperexcitadibility,seizures and coma.
8.	Cyprodinil	Organonitrogen	>2000	Inhibit action of cholinesterase,distrupt nervous ,system.
9..	Difenacoum	Rodenticide	1.8-2	Nausea, vomiting, anticoagulant poisioning.
10.	Fenoxycarb	Carbamate	10,000	Carcinogenic, skin and eye irritation ,allergic.
11	Carbofuran	Carbamate	6-18	Nausea, dizziness, respiratory paralysis, increased blood pressure.
12.	Propoxur	Carbamate	40	Inhibit action of cholinesterase,distrupt nervous system.
13.	Bitertanol	Triazole	5000	Effect central nervous system , sedation, spasms, respirator disturbance.

14.	Parathion	Organophosp-hate	3	Carcinogenic, Depression, speech difficulties, sleep walking.
15.	Profenophos	Organophosphate	867.50	Inhibit action of cholinesterase,distrupt nervous system.
16.	Diquat	Ethyl bipyridyl	120	Neurological effect, mouth, ,throat infection.
17.	Hexazinone	Triazine	1690	Damage liver and heart , tremors.
18.	Pentachloro Phenol	Organochloro Compound	27	Eye and nose irritation, carcinogenic, mutagenic and neurotoxic.
19	Monocrotophos	Organophosphate	23	Inhibit action of cholinesterase,distrupt nervous system.
20	Mancozeb	Carbamate	>5000	Reproductive and developmental toxicity, neurotoxicity and acute toxicity.
21	Phosphamidon	Organophosphate	9/367	Affect central nervous system, involountarymuscle concentration,paralysis of body extremities and respiratory muscles.
22	Maneb	Carbamate	5000-8000	Goiter, reduce growth rate, gastrointestinal disturbances.

References :

1. Aktar, M.W. Sengupta, D. Chowdhury, A. " Impact of pesticides use in agriculture: their benefits and hazard". *Interdisciplinary Toxicology* **2009** 2: 1-12.
2. Michael, C.R. Alavanja, J. A.H. and Freyn, K. "Health effects of chronic pesticides Exposure; Cancer and Neurotoxicity"*Annual review of public health*. **2004** 25: 155-197.
3. Tadeo, J.L. " Analysis of Pesticides in Food and Environmental Samples", CRC Press, Boca Raton, **2008**.
4. De, A.K. "Environmental Chemistry" *New age New Delhi India*.,**2007** 6:98-103.
5. Miyamoto, "The chemistry, metabolism and residue analysis of synthetic Pyrethriods.", *Journal of Pure and Applied Chemistry* **1981** 53:1967-2022.
6. Bradman, M.A. Harnly, M.E. Draper, W. Seidel, S. Teran, S. Wakeham, D. Neutra, R. "Pesticide exposures to children from California's Central Valley: results of a pilot study." *Journal of Exposure Analysis and Environmental Epidemiology* **1997** 7(2):217–34
7. Kolaezinski, J. H. Curtis, C.F. "Chronic illness as a result of low- level exposure to synthetic pyrethriod insecticides: a review."*Food and Chemical Toxicology*. **2004** 42:647-706.

8. Michael,C.R.Alavanja,Jane,A.H.Kamel,F. "Health effects of chronic pesticide exposure:Cancer and Neurotoxicity." *Annual Review of Public Health*. **2004** 25: 155-197.
9. Scotsman, E. "Pesticides a cancer risk to the unborn, say scientists" .,h*ttp: // newsletters environmental health news.org*/t/42238 /26628 /51996/01., **2010**.
10. Minf W., Hassine A.I.H., Bouaziz A., Bartegi A., Thomas.O., and Roig B., "Effect of endocrine disruptor pesticides a review.", *International Journal of Environmental Research and Public Health*. **2011.**
11. "Indian Pesticides Industry", *Market research Report*, September **2011.**
12. "Directorate of Agriculture", *Indira Gandhi Agriculture University, Raipur (C.G.),*Annual Report. **2011.**
13. Jiang, W. Gan, J. and Haver, D. *Environmental Science and Technology*. **2011** 45: 602-607.
14. Bakar, N.A.Salleh, M.M.Umar, A.A. and Yahaya, M. "The detection of pesticides in water using ZnCdSe quantum dot films."*Advance in Natural Science Nanoscience and Nanotechnology* **2011** 2:25011.
15. Araound, M. Douki, W. Najjar, M.F. and Kenani, A. " Simple analytical method for determination of pesticides residues in human serum by liquid chromatoghraphy tandem mass spectrometry." *Journal of Environmental Science and Health* **2010** 45: 242-248.
16. Lin, J. Chen, D. Chen, J. and Chen, Y. "Multilayer gold nanoparticle assisted thermal desorption ambient mass spectrometry for the analysis of small organic." *Analyst* **2010** 135, 2668-267.
17. Sharma,D.Nagpal,A. Pakade,Y. B. and Kanoria, J. K. *"*Analytical methos for estimation of organophosphorus pesticides residues in fruits and vegetable : A review.*" Talanta* **2010** 82: 1077-1089.
18. Portoles, T. Sancho, J. V. Hernandez, F. Newton, A. and Hancock, P. "Potential of atmospheric pressure chemical ionization source in GC-QTOF Ms for pesticide residue analysis.", *Journal Mass Spectrometry*. **2010** 45, 8, 926-936.
19. Matamoros, V. Jover, E. and Bayona, J. M. "Part- per-trillion determination of pharmaceuticals, pesticide, and related organic contaminants in river water by solid phase extraction followed by comprehensive Two-dimensional gas chromatography time-of flight mass spectrometry." *Journal Mass Spectrometry* **2010** 82,699-706.
20. Tang, S. J. Zhang, M. Cheng, C.G. and Lu, Y. T. "Development of fluorescence polarization immune assay for the detection of the organ phosphorus pesticide parathion and azinophos- methyl." *Journal of Immunoassay Chemistry* **2008** 29: 356-369.
21. Shivhare, P.Gupta, V.K. *Microchemical journal*, **1990** 42:283.
22. Shivhare, P.Gupta, V.K. *International Journal of Environmental and Analytical Chemistry*. **1991** 1097.
23. Kesari, R. Gupta, V.K. *J. of AOAC. Int*.,**1997** 80:388-399.
24 Kesari, R. Gupta, V.K. *J. of Indian Chemical Society.*, **1998** 96,250.
25. Raju, J. Gupta, V. K. *J. of Indian Chemical Society.*,**1989** 66,358.
26. Raju, J. Gupta, V. K. *Asian Environment*,. **1988** 10:45.
27. Khan, S. Rai, M.K. Gupta, V.K. Janghel, E.K. and Rai, J.K. *J.Chemical Society of Pakistan* .,**2007** 29(1): 37-40.

List of Published/Communicated/ Presented papers :

1) A paper entitled "A New Extractive Solid Sorbent System For Determination of Diquat" has been presented as poster in National Conference on Interaction Between Traditional and Morden Technology (NCITMT- 2012) C.G. at Rajya Gramin Vikas Sansthan,Nimoram Raipur (Chhattisgarh) India, on 24-25 March- 2012. **(Best poster presentation award.)**
2) A paper entitled "A New Spectrophotometric method for the determination of baygon in Environmental and Biological Samples" has been presented in National Conference on Biological Science in Current Scenario at ST. Thomas College, Bhilai (C.G) India on 10th October 2012.
3) A paper entitled "Extractive Spectrophotometric Determination Of Baygon In Environment And Biological Samples." has been presented in International Conference on Environment and Human Health organized by National Environmental Science Academy in association with Department of Botany, Jamia Hamdard at Indian National Science Academy, New Delhi, India on 28-29th November 2012.
4) A paper entitled "A New and Highly Sensitive Spectrophotometric Method for the Determination of Chlorpyrifos in Various Environmental and Biological Samples." Has been presented in 49th Annual Convention of Chemist 2012 at Department of Applied Science, National Institute of TechnicalTeachers Training and Research, Shamla Hills,Bhopal, (Madhya Pradesh) India on 12-15th December 2012**. (Young Scientist Award - Upadhyayulu Annapurna & Satyanarayana Memorial award.)**

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